APPENDIX - I

PUBLICATIONS

Palladium doped manganese dioxide catalysts for low temperature carbon monoxide oxidation
A. V. Salker and R. K. Kunkalekar

Low temperature carbon monoxide oxidation over nanosized silver doped manganese dioxide catalysts
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Activity of Pd doped and supported Mn_2O_3 for CO oxidation reaction
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Communicated

Nano-sized Cu-Pd doped and supported MnO_2 catalysts for lower temperature catalytic CO oxidation reaction
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Preparation, characterization and solid state studies on Ni doped Mn$_2$O$_3$ nanomaterials
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Preparation of Ce doped Mn$_2$O$_3$ catalysts for CO oxidation
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Preparation characterization of Ni doped MnO$_2$ nanomaterials
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Preparation and characterization of Ag doped Mn$_2$O$_3$ catalysts for CO oxidation
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Carbon monoxide oxidation over doped manganese dioxide catalysts
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Preparation and characterization of Pd doped Mn$_2$O$_3$ catalysts for CO oxidation
R. K. Kunkalekar and A. V. Salker

Preparation and characterization of doped manganese dioxide materials and their catalytic activity for CO oxidation reaction
R. K. Kunkalekar and A. V. Salker
Palladium doped manganese dioxide catalysts for low temperature carbon monoxide oxidation

A.V. Salker*, R.K. Kunkalekar
Department of Chemistry, Goa University, Goa 403206, India

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1. Introduction

Carbon monoxide (CO) is one of the toxic components of industrial waste gases and exhaust gases from automobiles. It is also formed in the regeneration of hydrocarbon cracking catalysts. It causes potential harmful effects on living beings and environment. Thus complete elimination or abatement below the permissible levels fixed by environmental regulations is a major concern. In recent years many methods have been used to reduce the emissions of CO. The catalytic technologies are attractive because of their low cost and high efficiency. Nanotechnology has recently experienced a rapid escalation owing to the unique physical and chemical properties of nanoparticles compared with the bulk solids [1-4].

Many different catalysts have been prepared and tested for the low temperature carbon monoxide oxidation activity. Precious metals like Pt, Pd, Au, Rh, Ru are active catalyst for CO conversion [5-7]. They generally allow low operating temperatures and higher space velocities than the transition metal oxide based catalysts. However, due to the high cost of noble metals and their less availability as well as sublimation and sintering problems, considerable part of the research has been devoted to the development of suitable catalyst among the transition metal oxides [8-10]. Appropriate combination of oxides and some mixed metal oxides exhibit greater activity and thermal stability then the single oxides. Combination of noble metals with transition metal oxides result in materials with high catalytic activity, stability and also require less quantity of the noble metals [11-14]. Few reports are available on palladium supported catalysts, indicating that they are very active and stable. Palladium is used as catalyst in various types of reactions [15-18]. Manganese dioxide is an important material widely used as a catalyst [19-22], cathodic material in batteries [23,24] and in organic synthesis. The properties of MnO2 are influenced significantly by its structure, morphology and preparative methods. The basic building block of manganese oxide is MnO6 octahedra, these octahedra share their corners or edges into variety of different structural arrangements [25,26]. A great deal of attention has been paid to the preparation of MnO2 with different crystallographic structures and morphologies [25-28].

In the present investigation, a series of nano-sized Pd doped MnO2 catalyst were prepared by dextrose aided co-precipitation technique. The prepared catalysts were tested for CO oxidation reaction and other studies. The interaction of Pd with MnO2 results in materials with high catalytic activity, stability and also require less amount of palladium [11-14]. Few reports are available on palladium supported catalysts, indicating that they are very active and stable. Palladium is used as catalyst in various types of reactions [15-18]. Manganese dioxide is an important material widely used as a catalyst [19-22], cathodic material in batteries [23,24] and in organic synthesis. The properties of MnO2 are influenced significantly by its structure, morphology and preparative methods. The basic building block of manganese oxide is MnO6 octahedra, these octahedra share their corners or edges into variety of different structural arrangements [25,26]. A great deal of attention has been paid to the preparation of MnO2 with different crystallographic structures and morphologies [25-28].

In the present investigation, a series of nano-sized Pd doped MnO2 catalyst were prepared by dextrose aided co-precipitation technique. The prepared catalysts were tested for CO oxidation reaction and other studies. The interaction of Pd with MnO2 results in materials with high catalytic activity. The effect of moisture was studied to see the performance of the catalyst for CO conversion along with activity test.

2. Experimental

2.1. Catalyst preparation

The solid catalysts of composition Mn1−xPdxO2 (where X = 0, 0.02, 0.05, 0.08) were prepared by dextrose aided co-precipitation technique. All reagents used were of analytical grade. Appropriate amount of manganese (II) acetate was dissolved in distilled water at room temperature, calculated amount of palladium (II) chloride
was taken in a separate beaker, to this distilled water and concentrated nitric acid was added and heated with stirring to dissolve completely. Both these solutions were mixed together at room temperature to get a clear homogeneous solution. This solution was added to 2% dextrose solution at 100 °C with constant stirring. The mixture was allowed to cool down to room temperature and then filtered. The precipitate was washed with distilled water to remove any traces of nitric acid. The precipitate was then dried in an oven at 120 °C for 10 h. Finally the dried precipitate was homogenized well in mortar and calcined in air at 400 °C for 5 h.

2.2. Catalyst characterization

The X-ray powder diffraction (XRD) measurement was carried out on RIGAKU diffractometer, using Cu Kα radiation (\(\lambda = 1.5418\) Å). The BET surface area was measured by nitrogen adsorption at liquid nitrogen temperature using a SMART SORB-91 surface area analyzer. The samples were degassed at 200 °C for 4 h prior to the adsorption experiments. The surface morphology was determined with JSM-5800LV scanning electron microscope (SEM) instrument operating at 20 kV. Thermal analysis was carried out on a NETZCH STA 409 PC TG/DSC instrument in air at a heating rate of 10 K min\(^{-1}\) and heated from ambient to 1100 °C.

2.3. Catalytic activity

The catalytic tests for CO oxidation by \(\text{O}_2\) were carried out in a continuous flow, fixed bed glass reactor. The catalyst powder of 0.9 g was supported between glass wool plugs in a glass reactor which was placed in an electric furnace. The catalytic activity was determined using a feed gas composition of 5% CO and 5% \(\text{O}_2\) in nitrogen. All these three gases were first mixed in a mixing bulb. The individual gas flow rates were controlled using flow meters and precision needle valves, previously calibrated for each specific gas. The mixture of gases was then allowed to pass over the catalyst at a rate of 5000 ml h\(^{-1}\). The temperature of the furnace was raised slowly from room temperature to the temperature at which 100% CO conversion is achieved. The feed gases and the products were analyzed in the laboratory by standard procedure and further purified by passing through alkali and molecular sieve traps. Oxygen, nitrogen and hydrogen gases were used from pure commercial cylinders.

The activity of the catalysts was tested for CO oxidation continuously for 5 h, by keeping the catalyst at a constant temperature. Also the effect of moisture on the catalytic activity was studied with low and high moisture contents at a fixed temperature.

3. Results and discussion

3.1. Characteristic properties

Fig. 1 shows the XRD pattern for \(\text{MnO}_2\) and \(\text{Mn}_{0.92}\text{Pd}_{0.08}\text{O}_2\). The peaks were assigned for \(\text{MnO}_2\) at the 20 angles of 37.34° (1 3 1), 38.42° (2 3 0), 42.3° (3 0 0), 56.22° (1 6 0) and 65.04° (4 2 1) shown in Fig. 1a. All the reflections of the XRD patterns can be readily indexed to \(\text{MnO}_2\) which agrees well with the values reported in literature (ICDD Card No. 14-0644). Whereas the XRD phase identification of \(\text{Mn}_{0.92}\text{Pd}_{0.08}\text{O}_2\) revealed characteristic signals at 20 values of 34.04° (1 3 0), 36.04° (0 2 1), 55.03° (2 2 1) and 60.34° (2 3 1) which is shown in Fig. 1b and these reflections correspond to the ramsdellite structure of \(\text{MnO}_2\) (ICDD Card No. 05-0600). Pd doped samples exhibits ramsdellite structure of \(\text{MnO}_2\).

The BET surface area of prepared samples is listed in Table 1. \(\text{MnO}_2\) shows surface area 44 m\(^2\) g\(^{-1}\). There is no decrease in surface area when palladium is doped in \(\text{MnO}_2\).

The surface morphology of the prepared catalysts was investigated by SEM and is shown in Fig. 2. From the SEM images it is observed that the particles are nano sized and in the range of 30–50 nm. Preparation of catalysts by co-precipitation technique in dextrose solution may highly influence the particle size, also not much agglomeration of particles is seen. Due to the addition of dextrose solution during preparation, the precipitated mixture does not get settled easily and they remain suspended in the solution. As a result, the particles got separated thus resulting in ultra fine, spherical nanoparticles.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) of \(\text{MnO}_2\) and \(\text{Mn}_{0.92}\text{Pd}_{0.08}\text{O}_2\) were carried out. All the samples showed the initial weight loss at 80–120 °C region which is generally due to loss of adsorbed water [28]. The weight loss in the region 560–700 °C is attributed solely to the loss of oxygen and this weight loss is generally considered due to the transformation of \(\text{Mn}_2\text{O}_3\) to \(\text{MnO}_2\) phase [29]. Further weight loss in the temperature range 880–1050 °C is due to the conversion of \(\text{Mn}_2\text{O}_3\) to \(\text{Mn}_3\text{O}_4\) phase.

3.2. Catalytic performance

Fig. 3 shows the catalytic performance for CO oxidation of the \(\text{MnO}_2\) and Pd doped \(\text{MnO}_2\) samples. From the figure it is clear that Pd doped catalysts show high activity for CO oxidation. It is observed that the light-off temperature (\(T_{50}\)) of Pd doped \(\text{MnO}_2\) catalysts are at a much lower temperature than that of \(\text{MnO}_2\).

<table>
<thead>
<tr>
<th>Sample</th>
<th>(T_{50}) (°C)</th>
<th>(T_{100}) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{MnO}_2)</td>
<td>130</td>
<td>200</td>
</tr>
<tr>
<td>(\text{Mn}<em>{0.98}\text{Pd}</em>{0.02}\text{O}_2)</td>
<td>87</td>
<td>110</td>
</tr>
<tr>
<td>(\text{Mn}<em>{0.92}\text{Pd}</em>{0.08}\text{O}_2)</td>
<td>76</td>
<td>115</td>
</tr>
<tr>
<td>(\text{Mn}<em>{0.92}\text{Pd}</em>{0.08}\text{O}_2)</td>
<td>69</td>
<td>50</td>
</tr>
</tbody>
</table>

\(T_{50}\) Temperature for 50% conversion for CO oxidation. 
\(T_{100}\) Temperature for 100% conversion for CO oxidation.
catalyst. The light-off temperatures of 50% CO conversion (T_{50}) and 100% CO conversion (T_{100}) over different catalysts are presented in Table 1. The addition of Pd in MnO_2 facilitates the adsorption of CO as well as O_2 which in turn shows higher activity. The MnO_2PdO_2 gave total conversion at around 90 °C which is to a great extent much lower as compared to MnO_2, indicating that Pd doped MnO_2 is an excellent catalyst for CO oxidation reaction.

Generally CO oxidation on transition metal oxides follows a mechanism proposed by Mars–Van Krevelen [30], implying that the lattice oxygen incorporation occurs during CO oxidation and that the reduced surface of the metal oxide is rejuvenated by taking up oxygen from the feed mixture [31]. On the other hand, it is well known that the reactivity for the structure sensitive reaction depends on the particle size, surface morphology and crystal plane of the catalyst [1]. Thus surface structure of the catalyst also influences catalytic performance.

Maximum CO conversion over metal oxide catalyst greatly depends on the method of preparation. The surface area largely depends on the preparative methods and higher the surface area generally corresponds to higher oxidation activity. Inspite of MnO_2PdO_2 having lower surface area it showed highest activity because Pd–MnO_2 interaction might have resulted into more active sites per unit surface area compared to other catalysts. It is seen that by introducing Pd in MnO_2 influences the activity of MnO_2 and 100% CO conversion is obtained at temperature of 90 °C, this gives evidence that by introducing Pd in MnO_2 produces a strong Pd–MnO_2 interaction which may be similar like the interaction in Ag–MnO_2 [1] and this interaction results in more favorable surface active sites which gives higher CO conversion at low temperature.

3.3. Activity test for the catalysts and effect of moisture on its activity

The activities of the catalysts MnO_2 and MnO_2PdO_2 were tested for CO oxidation continuously for 5 h by maintaining the temperature of the catalyst near to its 50% CO conversion temperature (T_{50}).

MnO_2 catalyst was maintained at a fixed temperature of 130 °C to check the activity. Around 50% CO conversion was observed in 1 h. After 5 h nearly 55% CO conversion is observed, indicating increase in activity with time. Fig. 4a depicts the results of the activity test. No decrease in activity of the catalyst was accounted during this period, signifying that MnO_2 catalyst is a good catalyst for CO conversion.

The activity of MnO_2PdO_2 was also tested for 5 h continuously. This test was performed to ascertain whether the activity of the catalyst retains with increasing reaction time or not. The catalyst was kept at a fixed temperature of 50 °C. With increase in the reaction time, the CO conversion remains almost constant with a slight increase. Fig. 4a shows the results of activity test. It was reported that palladium oxide powder shows high activity for CO oxidation even at room temperature [32], but its activity decreases with increasing temperature. But when MnO_2 was doped with Pd, a strong interaction occurs between Pd and MnO_2 which results in high catalytic activity. Even catalyst like Ag doped OMS-2 shows very low activity at 100 °C and its activity goes on decreasing with time [26].
The effect of moisture on the activities of MnO$_2$ and Mn$_{0.92}$Pd$_{0.08}$O$_2$ catalysts were tested. The activity was tested in the presence of low and high moisture content. The activity of the catalyst in the presence of low moisture content was tested by allowing the mixture of feed gases to pass through water trap (maintained at room temperature) before passing through the catalyst bed. At room temperature the number of water molecules passing along with feed gases is around $1.67 \times 10^{21}$ molecules h$^{-1}$. Also the activity of the catalyst was tested with high moisture content by allowing the mixture of feed gases to pass through water trap (maintained at 50 °C temperature) before passing through the catalyst, at 50 °C the number of water molecules passing along with feed gases is around $8.31 \times 10^{21}$ molecules h$^{-1}$. Also the activity of the catalyst was kept constant and activity was tested for 5 h continuously.

MnO$_2$ catalyst was kept at a fixed temperature of 130 °C, and then the mixture of feed gases coming from the water trap was allowed to pass through the catalyst bed. Under the influence of low moisture, after 1 h, nearly 52% CO conversion was observed. Later CO conversion was found to increase and after 5 h 58% CO conversion was observed as seen in Fig. 4b. This illustrates that the catalyst retains its activity under the influence of moisture and the results obtained in presence of moisture are much better than in absence of moisture. With increasing time of the reaction there is an increase in activity of the catalyst indicating optimistic effect of moisture on the MnO$_2$ catalyst. The effect of high moisture content on catalytic activity of MnO$_2$ shows much better results as compared to low moisture content. More CO conversion was observed under the influence of higher moisture content. After 1 h, 55% CO conversion was observed and it goes on increasing with reaction time. Around 61% CO conversion was seen after 5 h, thus by providing more amount of moisture along with feed gases, the activity for CO conversion was seen to increase as shown in Fig. 4c.

The Mn$_{0.92}$Pd$_{0.08}$O$_2$ catalyst was also tested to see the effect of moisture. The catalyst was kept at a fixed temperature of 50 °C. Under the influence of low moisture, after 1 h, 47% CO conversion was observed as shown in Fig. 5b and after 5 h it increases to about 58% showing increase in activity by roughly 10% after 5 h. The Mn$_{0.92}$Pd$_{0.08}$O$_2$ shows excellent CO conversion activity with higher moisture content. Around 60% CO conversion was seen after 1 h and with increase in the reaction time, it reaches to 78% after 5 h as seen in Fig. 5c. Consequently the activity of Pd doped MnO$_2$ is also highly influenced by passing moisture along with the feed gases and with more moisture it gives much better result. From these findings it is seen that the presence of moisture strongly influences the CO conversion activities over these catalysts. No deactivation is observed for CO oxidation reaction. Obviously, the reaction mechanism of CO oxidation by O$_2$ over these catalysts under the influence of moisture is likely to be different. Due to hydration of the adsorbed CO molecule, the CO bond is weakened significantly, which facilitates its oxidation [33] and presence of Pd highly influence this activity. Also water may increase the acidic sites on the surface of the catalyst [34] enhancing CO adsorption thus leading to higher activity.

4. Conclusions

The Pd doped MnO$_2$ catalysts showed high activity for CO oxidation and complete conversion was achieved at a much lower temperature as compared to MnO$_2$. The XRD pattern confirmed the formation of MnO$_2$ phase. SEM images shows that particles are nano sized and in the range of 30–50 nm. Thermal analysis gives evidence for the phase change of MnO$_2$ to Mn$_3$O$_4$ and Mn$_2$O$_3$ with increase in temperature. The activity test carried out at fixed temperature showed that the activity does not fall with time but show slight increase in the percentage conversions. The influence of moisture has enhanced the activity over these catalysts.

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References

Low temperature carbon monoxide oxidation over nanosized silver doped manganese dioxide catalysts

R.K. Kunkalekar, A.V. Salker *  
Department of Chemistry, Goa University, Goa 403206, India

ABSTRACT

Nanosized silver doped manganese dioxide catalysts have been prepared and tested for CO oxidation reaction at lower temperature. Silver doped manganese dioxide catalysts show higher CO conversion as compared to undoped manganese dioxide. Under the influence of excess oxygen catalysts are stable and show good activity. From time on stream experiments it is clear that the catalysts are highly stable for CO oxidation for a longer period in absence of moisture as well as in presence of moisture in the feed gas. The catalysts show higher activity for CO conversion in presence of moisture, indicating that moisture facilitates CO oxidation reaction on the catalyst surface.

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1. Introduction

The carbon monoxide is one of the main toxic gaseous pollutants which is generally produced and released from the combustion process of fossil fuels. Catalytic oxidation of carbon monoxide to carbon dioxide at low temperature has been of considerable interest due to its significance in many industrial applications as well as to meet stringent environmental regulations. Last several years various catalysts have been prepared and tested for lower temperature CO oxidation. Mixed metal oxides such as hopcalite [1,2], mixed cobalt-cerium oxides [3,4] and supported metal oxides have been found to be highly active for CO oxidation reaction.

Manganese oxides (MnO) have long been used as highly active, durable, low cost and environmental friendly catalysts for the combustion of various volatile organic substances [5–7]. Various types of manganese oxide, mixed manganese oxide, noble metal doped/supported Mn oxides [8,9] are widely used for CO oxidation reaction. Among all manganese oxides, MnO₂ is most important due to its unique properties and has wide applications in different fields. It is generally accepted that phase structure can significantly influence the catalytic activity of MnO₂ [10,11].

Presence of moisture in feed stream highly influences the activity of catalysts for CO oxidation reaction. Catalysts such as PtAu/CeO₂ [12] deactivates in the presence of moisture while catalysts like Au/TiO₂, Ir/TiO₂ [13,14] show good activity and stability in presence of moisture. In the present work, the development of a new efficient nanosized Ag doped MnO₂ catalyst exhibiting exceptionally high activity and enhanced stability for CO oxidation reaction is being discussed.

2. Experimental

2.1. Catalysts preparation

Nanosized Ag doped MnO₂ catalysts of the type Mn₁₋ₓAgₓO₂ (where x = 0, 0.02, 0.05, 0.10, 0.15 and 0.20) were prepared by co-precipitation and drying method. Stoichiometric amount of manganese acetate and silver nitrate were dissolved in distilled water. Both these solutions were added to 200 ml distilled water at 100 °C with stirring. Subsequently, the suspension was subjected to oxidation by drop wise addition of 30% H₂O₂ solution with constant stirring [15]. The suspension was then stirred continuously at 100 °C till dryness. The resulting product was dried at 150 °C for 6 h and calcined in air at 400 °C for 10 h.

2.2. Catalysts characterization

The phase composition of the calcined samples was analyzed by X-ray diffraction (XRD) using RIGAKU Ultima IV diffractometer. Transmission electron microscope (TEM) images were recorded on a PHILIPS CM 200 electron microscope. Elemental analysis was performed using energy-dispersive X-ray (EDX) on JEOL JSM 6360-LV scanning electron microscope and atomic absorption spectroscopy (AAS) on AA-6300 SHIMADZU. The BET surface area was measured by nitrogen adsorption at liquid nitrogen temperature using a SMART SORB 91 surface area analyzer.
2.3. Catalytic performance

The catalytic tests for CO oxidation by O2 were performed in a continuous flow, fixed bed glass reactor. The catalyst powder of 0.9 g was supported between glass wool plugs in a glass reactor. The catalytic activity was determined using a feed gas composition of 5% CO and 5% O2 in nitrogen and pass over the catalyst at a rate of 5000 ml h⁻¹. Prior to the CO oxidation reaction the catalyst was activated by passing O2 at 100 °C for 30 min. The feed gases and the products were analyzed employing an online gas chromatograph with molecular sieve 13X and Porapak Q columns. H2 was used as a carrier gas.

3. Results and discussion

3.1. Catalysts characterization

The XRD pattern of MnO2 (Fig. 1a) shows well defined diffraction features characteristics of nanocrystalline MnO2, indexed to tetragonal phase. After doping of Ag, an almost identical pattern was obtained for Ag doped MnO2 samples as that of pristine MnO2 indicating well maintaining of the crystal structure of MnO2. Fig. 1b and c shows the XRD patterns for Mn0.95Ag0.05O2 and Mn0.90Ag0.10O2 catalysts. No distinct Ag reflections are visible in the XRD patterns of any sample indicating that Ag is well incorporated in MnO2.

Representative TEM images of MnO2 and Mn0.95Ag0.05O2 catalysts are shown in Fig. 2. From the figure it is clear that the particles are nanosized and in the range 25–50 nm, the particles are agglomerated in appearance and spherical in nature. Inset in the figure shows electron diffraction patterns; Fig. 2a shows that rings are made of discrete spots signifying crystalline nature of MnO2. But in contrast, Ag doped MnO2 catalysts (Fig. 2b) exhibited clear continuous ring patterns demonstrating that Ag doped catalysts are polycrystalline in nature. From the EDX and AAS analysis of Mn0.95Ag0.05O2 it is confirmed that Mn and Ag are present in appropriate ratio. The weight % ratio of Mn/Ag found to be 9.9 which is almost close to theoretical value.

The specific BET surface area of all the catalysts has been summarized in Table 1. After incorporation of Ag in MnO2 the surface area found to be almost in the same range, but in the case of higher doped samples the surface area found to be decreased monotonously.

3.2. Catalytic activity

Fig. 3 displays the temperature dependence of the CO oxidation over various catalysts. It is clear that activity of the Ag doped MnO2 catalysts are much higher than that for the pure MnO2 catalysts. The T50 and T90 (light-off temperature of 50% and 100% CO conversion) values are given in Table 1. The pure MnO2 shows complete CO oxidation at 180 °C whereas Ag doped MnO2 catalysts show complete conversion below 125 °C. Moreover one can see that complete oxidation of CO could be attained at temperature 80 °C over Mn0.95Ag0.05O2 catalyst. Even the catalyst like Ag/MnO2 and Ag-Mn composite oxide shows complete CO conversion at higher temperature [16,17] than the present catalyst. The data in Fig. 3 also indicated that oxidation activity per catalyst increased monotonously with Ag doping, but for higher Ag doped samples the catalytic activity found to be decreasing.

As an electron donor, when CO molecule adsorbed on the surface of Ag, the C=O bond is activated by the back donation electrons from the filled d orbitals of Ag to CO 2π* antibonding molecular orbitals. In addition, incorporation of Ag produces a strong Ag–MnO2 interaction [16] which also promotes CO adsorption. XRD and TEM studies suggest that Ag is highly incorporated in MnO2 and probably interact strongly with MnO2.
Table 1
BET surface area and catalytic activity at different temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>SA (m² g⁻¹)</th>
<th>T₅₀ (°C)</th>
<th>T₁₀₀ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO₂</td>
<td>24</td>
<td>147</td>
<td>185</td>
</tr>
<tr>
<td>Mn₀.₉₅Ag₀.₀₅O₂</td>
<td>26</td>
<td>94</td>
<td>120</td>
</tr>
<tr>
<td>Mn₀.₉₀Ag₀.₁₀O₂</td>
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<tr>
<td>Mn₀.₇₀Ag₀.₃₀O₂</td>
<td>10</td>
<td>80</td>
<td>100</td>
</tr>
</tbody>
</table>

T₅₀ and T₁₀₀ (temperature for 50% and 100% CO conversion).

3.3. CO oxidation in excess oxygen

Performance of the catalysts for CO oxidation under the influence of excess oxygen i.e. 20% O₂ (5% CO and 20% O₂ in nitrogen) and 40% O₂ (5% CO and 40% O₂ in nitrogen) in feed gas mixture maintaining the same total flow rate of 5000 ml h⁻¹ was studied. No decrease in activity for CO conversion was observed under influence of 20% O₂, but instead it showed slight increase in activity. Also in case of 40% O₂, slight increase in activity was observed than that of 20% O₂. Thus the influence of excess oxygen favours CO oxidation reaction and shows better activity. The possibility of blocking of active sites for CO adsorption over the surface due to excess oxygen is not encountered.

3.4. Stability test for the catalysts

Time on stream studies were carried out on MnO₂ and Mn₀.₉₅Ag₀.₀₅O₂ catalysts for oxidation of CO continuously for 12 h. MnO₂ catalyst was maintained at 130 °C; from Fig. 4a it is clear that the catalyst is stable for CO oxidation for longer period and also increase in activity was observed. The Mn₀.₉₅Ag₀.₀₅O₂ catalyst was maintained at 60 °C, it also shows good stability and increase in activity (Fig. 5a). Comparatively, the Ag doped OMS-2 catalyst shows low activity at 100 °C and whose activity declines with increase in reaction time [18,19].

Thus the results of stability test shows that MnO₂ and Ag doped MnO₂ catalysts are highly stable for CO oxidation reaction. The basic building block for most of the manganese oxide is the MnO₆ octahedra [11], they are generally porous material and often crystallizes as microporous tunnel structures. This tunnel structure is necessary for high CO oxidation activity [18] and incorporation of Ag ions and their mobility may also play important role in CO oxidation.

3.5. Influence of moisture on activity of catalyst

The effect of moisture on the activities of MnO₂ and Mn₀.₉₅Ag₀.₀₅O₂ catalysts was also tested. The activity was tested in presence of low and high moisture content [15]. The activity of the catalyst in the presence of low moisture content was tested by allowing the mixture of feed gases to pass through water trap (maintained at room temperature) and in the presence of high moisture content by allowing the mixture of feed gases to pass through water trap (maintained at 50 °C) before passing through the catalyst bed.

MnO₂ catalyst was maintained at 130 °C. Under the influence of low moisture, MnO₂ catalyst is stable and shows increase in activity with time as seen in Fig. 4b. The effect of high moisture content on catalytic activity of MnO₂ shows much better results as compared to low moisture content. More CO conversion was observed, as shown in Fig. 4c.

The Mn₀.₉₅Ag₀.₀₅O₂ catalyst was maintained at 60 °C. Under the influence of low moisture, MnO₂ catalyst is stable and shows increase in activity with time as seen in Fig. 4b. The effect of high moisture content on catalytic activity of MnO₂ shows much better results as compared to low moisture content. More CO conversion was observed, as shown in Fig. 4c.

Thus the results of stability test shows that MnO₂ and Ag doped MnO₂ catalysts are highly stable for CO oxidation reaction. The basic building block for most of the manganese oxide is the MnO₆ octahedra [11], they are generally porous material and often crystallizes as microporous tunnel structures. This tunnel structure is necessary for high CO oxidation activity [18] and incorporation of Ag ions and their mobility may also play important role in CO oxidation.
One interesting phenomenon was observed during stability test, the activity of both the catalysts increases with time (Figs. 4 and 5) either in presence or in absence of moisture. The catalysts were maintained at lower operating temperature during the stability test (approximately near to its 50% CO conversion). At this low operating temperature the surface active sites which are responsible for CO adsorption may not be totally activated. With increase in time the surface active sites may get activated resulting in more CO conversion. But for longer time period this trend may not continue and expected to reach a plateau region of CO conversion.

From Figs. 4 and 5 it is clear that catalysts are stable for CO oxidation, and under the influence of moisture catalysts show higher activity. This gives evidence that moisture does participate in catalytic CO oxidation. In addition to normal catalytic reaction of CO with oxygen to produce CO$_2$, there is a possibility of adsorbed CO reacting with adsorbed OH$^-$ [20]. Water adsorbs dissociatively on catalyst surface as OH$^-$ and H$^+$, and then the hydroxyl group may combine with CO to form an intermediate, which then decomposes giving CO$_2$ and hydrogen. Also there may be a possibility of formation of Bronsted acid sites due to the adsorption of moisture on surface of the catalysts [21]. These acid sites will favour more adsorption of CO on surface of the catalyst which results in more CO$_2$ formation, thus showing better activity.

4. Conclusion

Ag doped MnO$_2$ catalysts showed high catalytic activity for CO oxidation reaction as compared to pristine MnO$_2$ and these catalysts are highly stable. Presence of moisture in the feed facilitates catalytic CO oxidation. X-ray diffraction patterns of silver doped manganese dioxides are almost similar to pure manganese dioxide indicating Ag is well incorporated in MnO$_2$. TEM images confirmed that the particles are nanosized.

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